

Ultrasonic velocity studies on the phase transition in 4-cyano-4'-n-hexyloxybiphenyl liquid crystal at 2 MHZ

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A study of liquid crystals is fascinating due to the complex theoretical aspects of their behaviour and a vast number of practical applications. Ultrasonic methods have been used in the study of liquid crystals in recent times. A study of temperature-dependence of physical properties, such as, ultrasonic velocity and derived parameters such as, adiabatic compressibility (β_s), molar sound velocity or Rao number (R), molar compressibility or Wada constant (B), gives information regarding the molecular structure, the nature of the phase transitions and pre-transitional effects in the vicinity of phase transition. In spite of many ultrasonic investigations in thermotropic liquid crystals, the information available on the behaviour of alkyl and alkoxybiphenyls is scanty (Natale 1978). The alkyl and alkoxybiphenyls are used with various other liquid crystals in displays (LCD systems). The anomalous behaviour of ultrasonic velocity in octyloxy cyanobiphenyl (8 OCB) with temperature around smectic-nematic (S-N) and nematic-isotropic (N-I) transitions was reported (Srinivasa Manja and Srinivasa Rao 1988). With a view to explore the behaviour of this class of liquid crystals, ultrasonic studies were carried out on 4-cyano-4'-n-hexyloxybiphenyl (6 OCB) liquid crystal which is a member of the homologous series of alkoxybiphenyls. The current work reports the ultrasonic behaviour of 6 OCB liquid crystal.

The liquid crystal 6 OCB used in the present work is supplied by BDH-England. Ultrasonic velocity was determined at various temperatures in the range 64-82°C at a frequency of 2 MHZ and at 2°C temperature-intervals using a continuous wave, variable-path interferometer. The accuracy in the measurement of velocity is ± 0.15 m/s. Density studies which throw light on the nature of phase transition, also carried out using a dilatometer in the same temperature range. The desired temperatures of the liquid crystals were maintained by circulating water from a thermostatically controlled water bath ($\pm 0.1^\circ\text{C}$).

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Using the ultrasonic velocity (C) and density data, parameters like adiabatic compressibility (β_s), molar sound velocity (R), molar compressibility (B) were calculated using standard formulae as reported elsewhere (Velmourougane et al 1987). The values are presented in Table 1. The variation of velocity and adiabatic

Table 1. Ultrasonic velocity and related parameters for liquid crystal 6 OCB.

T °C	C ms ⁻¹	$\rho \times 10^{-3}$ Kg m ⁻³	$\beta_s \times 10^{10}$ m ² N ⁻¹	$R \times 10^6$ m ^{10/3} s ^{-1/3}	$B \times 10^{22/7}$ m ^{20/7} Kg ^{1/7} s ^{-2/7}
64	1404	1.0253	4.9478	3047	216.5
66	1396	1.0229	5.0164	3048	216.6
68	1392	1.0210	5.0547	3051	216.8
70	1375	1.0191	5.1901	3044	216.4
72	1369	1.0176	5.2434	3044	216.4
74	1344	1.0161	5.4484	3030	215.5
76	1310	1.0123	5.7564	3016	214.6
78	1359	1.0104	5.3588	3059	217.3
80	1352	1.0074	5.4306	3062	217.5
82	1347	1.0049	5.4846	3066	217.7

T=Temperature; C=Ultrasonic velocity; ρ =Density of the liquid crystal; β_s =Adiabatic compressibility; R=Molar sound velocity; B - Molar compressibility.

compressibility with temperature are presented graphically in Figures 1A and 1B. The variation of density with temperature is presented in Figure 2. The plot of molar sound velocity and molar compressibility with temperature is presented in Figures 3A and 3B. Figure 1A shows the variation of ultrasonic velocity of 6 OCB in the temperature range 64°C-82°C in steps of 2°C. It is seen that the ultrasonic velocity increases as the temperature decreases from 82°C to 78°C. The ultrasonic velocity is found to be minimum at 76°C below which the velocity is found to increase with the temperature. A sharp decrease in the velocity as the temperature falls from 78°C to 76°C probably indicates a transition from isotropic state to nematic state. As the temperature decreases in the isotropic state, the mean distance between the molecules also decreases thereby increasing the potential energy of interaction between the molecules. This explains the increase in velocity with decrease in temperature in the isotropic state till transition occurs (Kapustin and Zvereva 1966). The sharp decrease in ultrasonic velocity in the vicinity of the isotropic-nematic phase is due to the transition from the disordered isotropic liquid phase to a more ordered nematic phase in which molecules tend to align parallel to each other. The density of the liquid fluctuates during the transition from

disordered isotropic phase to partially ordered nematic phase which may cause a decrease in velocity (Gabrielli and Verdini 1955, Otia and Padmini 1973, Pisipati and Rao 1982). Below the transition i.e., in nematic state the intermolecular

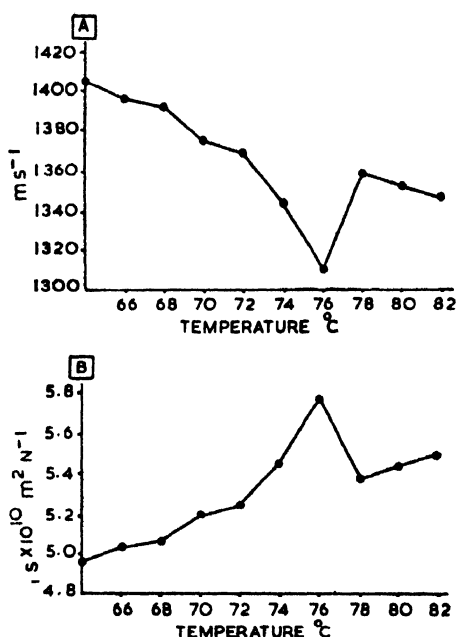


Figure 1. Ultrasonic velocity vs temperature (A) and adiabatic compressibility vs temperature (B) of 6 OCB.

distance decreases with decrease in temperature thus leading to a close packing of the molecules which explains the increase in ultrasonic velocity. Similar results are

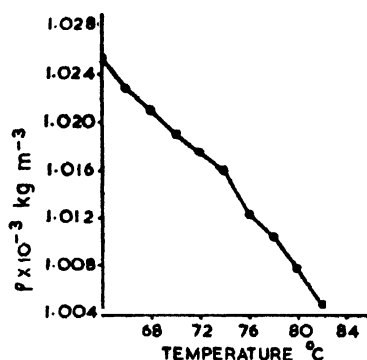


Figure 2. Density vs temperature of 6 OCB.

obtained in the studies of N-(p-n-hexyloxybenzylidene)-p-n-butylaniline (HBBA) and N-(p-n-pentyloxy benzylidene)-p-toluidine (Rao et al 1983). The studies on 8 OCB also support the results obtained in the present work (Srinivasa Manja and Srinivasa Rao 1988). The adiabatic compressibility shows a significant maxima near the phase

transition temperature (Figure 1B). In the vicinity of phase transition, a heterophase is expected which leads to vigorous fluctuations. The maximum fluctuations in the medium lead to maximum compressibility or a minimum in the ultrasonic velocity which is observed in the present system. This is in consistence with the Frenkel's heterophase fluctuation theory (Frenkel 1955). Frenkel has shown by analysis that as the temperature of a first order transition is approached an ever increasing concentration of small elements of the second phase can exist in the first phase. From Table 1 and Figure 2, it is seen that the density change around the transition temperature (74°C - 78°C) is small

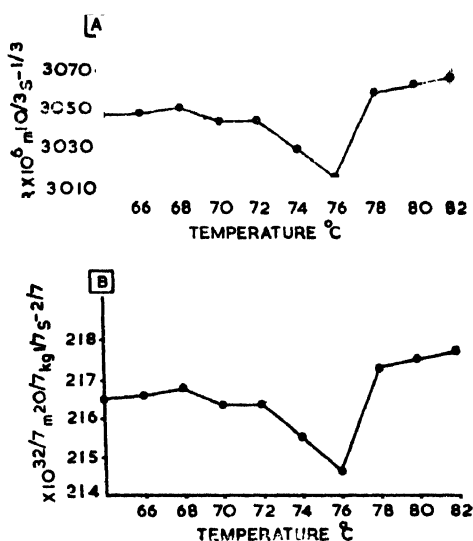


Figure 3. Molar sound velocity vs temperature (A) and molar compressibility vs temperature (B) of 6 OCB.

($0.0057 \times 10^8 \text{ Kg m}^{-3}$) which indicates a N-I transition (Otia and Padmini 1973). The observed density jumps at N-I transition of 0.56% indicates a first-order transition (Pisipati and Rao 1984). This view is further confirmed by the studies of Delaye (1976), who reported a weak first-order transition in 8 OCB which is a homologue of 6 OCB. From Table 1 and Figure 3 it can be seen that the molar sound velocity or Rao number (R) and molar compressibility or Wada constant (B) show a minimum value at the transition temperature. A dip of $43 \times 10^{-8} \text{ m}^{10/3} \text{ s}^{-1/3}$ was observed in molar sound velocity or Rao number at the N-I transition. It can be also seen from Table 1 and Figure 3 that the molar compressibility is minimum at N-I transition. The transition is thus indicated by a minimum in these values. Similar changes were observed in MBBA (Otia and Padmini 1973), HYBBA (Pisipati and Rao 1982), HBBA (Rao et al 1983) in the isotropic-nematic transitions. The crystal-nematic (K-N) phase transformation

which is expected below 64°C of this 6 OCB liquid crystal could not be mapped (as the compound is in a solid state) due to the difficulty of using a single apparatus without modification on both liquid and solid samples.

From the studies made, it can be concluded that the liquid crystal 6 OCB exhibits pre-transitional variations showing a dip in ultrasonic velocity, molar sound velocity and molar compressibility at the transition temperature. The pre-transitional behaviour can be understood on the basis of Frenkel's hetero-phase fluctuation theory (Frenkel 1955). Small changes in density around transition temperature confirms a first-order phase transition.

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